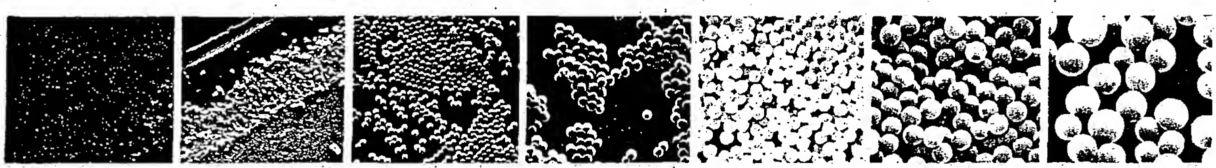
APPENDIX 1

esprit
A New Spirit in Partnership

Acrylic Ultra-fine Powder MP series

The MP series is a group of unique products originally developed by Soken. The material these products are made of is unique too, incorporating the function of both acrylic resin and ultrafine particles.



0.05μm 0.15μm 0.25μm 0.4μm 0.6μm 0.8μm 1–2μm

General description

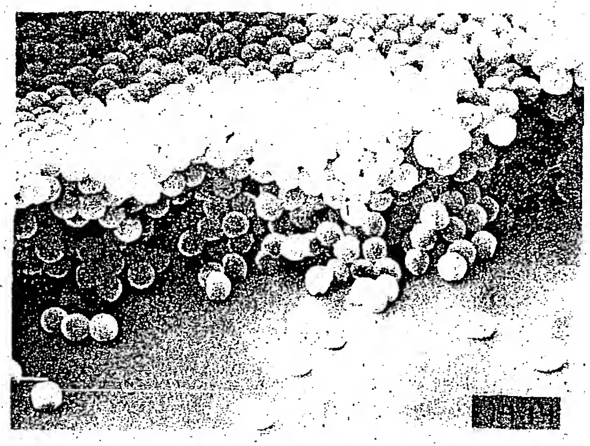
Acrylic polymer is a multifunctional polymer that offers wide applications due to the large choice of monomers, the numerous combinations available and the easy introduction of functional groups. In particular, acrylic ultrafine powder is a new material formulated to possess the functions of both acrylic resin and ultrafine particles.

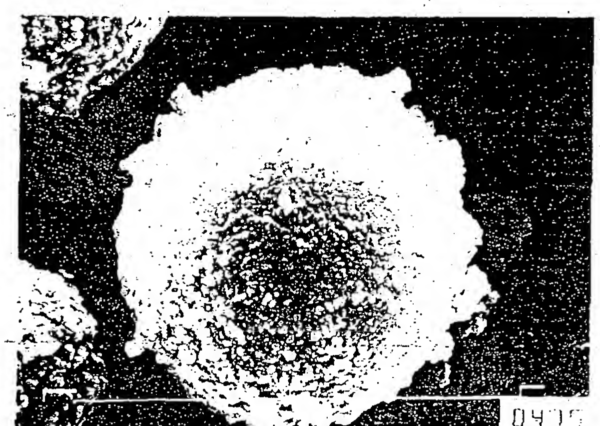
Development of the MP series of acrylic ultrafine powder products was pioneered by Soken using its own technology to make better use of submicron particle functions. These unique products are the result of applying long-studied techniques to acrylic polymerization and ultrafine powder production.

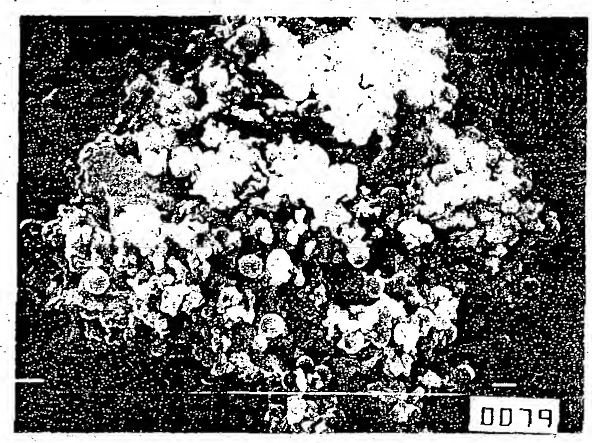
Recently, ultrafine particles have attracted a great

deal of attention in fields dealing with materials in powder form. Potential applications include improvers for enhancing powder mixing and flow characteristics and surface modifiers for making powders adhere to one another through the charging phenomena. New materials are expected to be developed using microencapsulation techniques based on *the dry powder-to powder mixing system.*

We believe that the acrylic ultrafine powder MP series meets the needs of the high-tech age and satisfies the demands of our customers.







Characteristics

The MP series consists of very loose particles that constitute ultrafine powder which makes the particles disperse readily in various types of powder such as organic powders, including plastics, pigments, ceramics and metal powders that are simple to mix.

The excellent dispersion is attributable to the charging phenomena that is unique to acrylic ultrafine powder. The MP series was specially formulated to bring out these characteristics and to meet specific applications.

Advantages

1. The surface of the particles is treated to produce both positive and negative charging so as to achieve maximum dispersibility.
2. The particles are untied.
3. The particles are polymerized without the use of surfactant to prevent the invasion of water even in high humidity.
4. The surface of the particles is treated to produce hydrophilia, lipophilia and reactivity when necessary.
5. The particles are adjusted for softening point, molecular weight, structure and composition to meet different applications. The properties of MP-1000, a representative product, are shown below.

Table 1 shows a list of acrylic ultrafine powder products. They include organic solvent-resistant products, those that form films at low temperature, and those that are treated with silica, as well as those with controlled friction and electrification and those with controlled particle diameters.

Grade Number	Characteristic					remarks
	particle size	polymer type	charge polarity	hydrophilic property	hydrophobic property	
MP-1000	0.4 µm	PMMA	−	o		
MP-1100	0.4	PMMA	−	o		
MP-1201	0.4	PMMA	−	o		
MP-1400	1~2	PMMA	−	o		
MP-1401	0.8	PMMA	−	o		
MP-1450	0.25	PMMA	−	o		
MP-1451	0.15	PMMA	−	o		
MP-1220	0.4	PMMA	−	o		silica coating
MP-2701	0.4	PMMA	+	o		cosmetic, medical
MP-3100	0.4	PMMA	−		o	solvent resistance
MP-4009	0.4	P-(MMA/BMA)	−		o	low softening point

Table 1 A list of acrylic ultrafine powder products

Characteristics of acrylic ultrafine powder

Properties and nature

Table 2 shows the properties of the representative product MP-1000. Figures 1, 2, and 3 and Table 3 show the molecular weight distribution, thermal properties, the distribution of grain size, and solubility in organic solvents.

The hydrophilic products listed in Table 1 give rise to suspension with good dispersion stability, when they are redispersed in water.

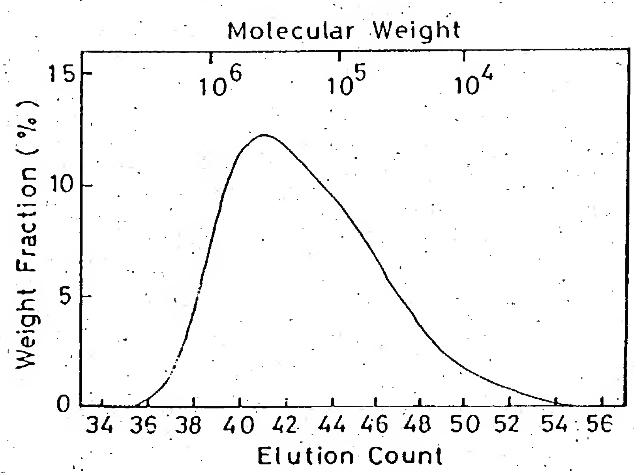


Fig. 1 GPC curve for MP-1000

	MP-1000
Appearance	fine white powder
Particle size	0.4 ~ 0.5 μm
Composition	polymethyl-methacrylate
Molecular weight	250000 ~ 500000
Glass transition temperature	120 ~ 130 °C
Thermal degradation temperature	200° C (1% weight loss)
Percentage of water content (%)	less than 2
Bulk density (ml/g) (JIS K 5101)	9 ~ 11
Oil absorption (ml/100g)	68±2
PH	6 ~ 7

Table 2 Physical properties of MP-1000

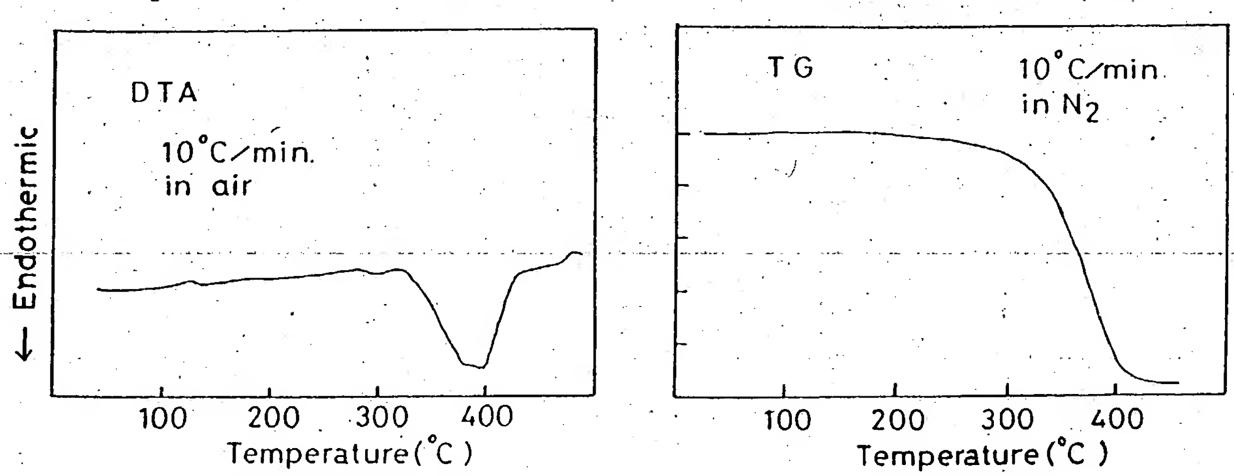


Fig. 2 Differential thermal analysis and thermal gravity analysis for MP-1000.

Particle size distribution of MP-1000
measured by MICRON PHOTO SIZER

Temp.	25°C
Dispersion medium	water
Dispersion condition	ultrasonic irradiation

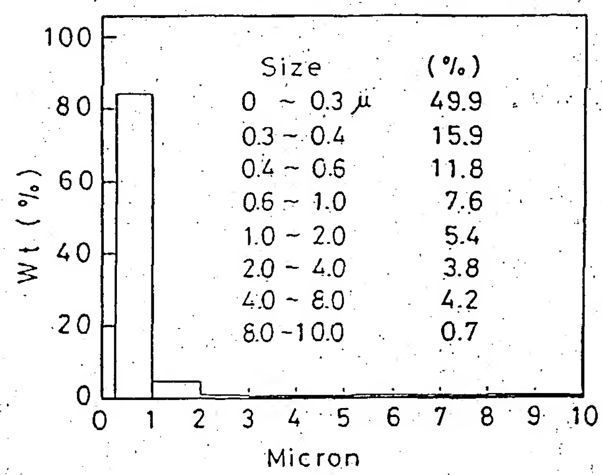


Fig. 3. Size distribution of MP-1000

Solvents	Solubility
n-Hexane	×
Cyclohexane	×
Toluen	○
Xylene	○
MEK	○
MIBK	○
Ethyl acetate	○
Butyl acetate	○
Chloroform	◎
Carbon tetrachloride	△
Acetone	○
THF	◎
Methyl cellosolve	○
IPA	×
Methacrylic acid	○
MMA	○
n-BMA	△
BA	○
2-EHA	×
ST	◎
HEMA	○

◎ easily soluble ○ soluble
△ hardly soluble × insoluble

Table 3 Solubility for various solvents

(1) Electrification of PMMA powder

Photograph 1 shows the SEM photographs of a mixture of iron and PMMA powders before and after blowing off. A light mix attaches PMMA powder to the surface of the iron powder in a uniformly isolated state. Most PMMA powder particles are blown off, except for part of the PMMA powder that remains in the recesses on the surface of the iron powder. Table 4 shows the characteristics of the samples used. Figure 5 shows the changes in electrification using varied mixing ratio of iron and PMMA powders. A smaller PMMA powder ratio produced lower electrification per unit weight Q/m; maximum Q/m was obtained with 1~3 mg/g. When the ratio of PMMA powder exceeded this, the Q/m value tended to decrease.

(2) Electrification of PMMA powder mixture with positive and negative electrification characteristics

Figures 6 and 7 show changes in electrification found when negatively charged N-1 or N-2 was mixed with positively charged P-1 powder. As the mixing ratio of N-1 or N-2 powder χ increased, the electrification ηm became negative, resulting in the following equations:

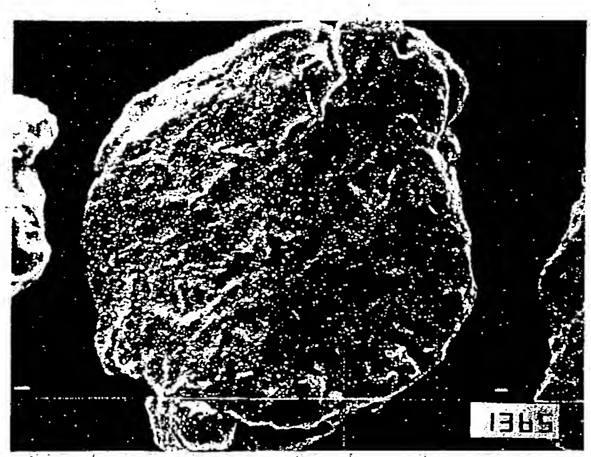
$$\eta m = \eta_{PI}\chi_{PI} + \eta_{NI}\chi_{NI} \qquad (3)$$

$$\text{or } \eta m = \eta_{P2}\chi_{P2} + \eta_{N2}\chi_{N2} \qquad (4)$$

Factors η_{PI}, η_{NI}, and η_{N2} represent the contact electrification of P-1, N-1, and N-2 powders alone and mixed with iron powder.

Factors χ_{PI}, χ_{NI}, and χ_{N2} represent the mixing ratio of P-1 to N-1 and P-1 to N-2; $\chi_{PI}+\chi_{NI} = 1$ and $\chi_{PI}+\chi_{N2} = 1$.

Equations (3) and (4) are indicated by dotted lines in Fig.s 6 and 7. The contact electrification of a mixture of two types of PMMA powder with different polarities to iron powder is expressed by the sum of the contributions of each type of PMMA powder to electrification, which developed additivity. This may be due to the following: 1) P-1 powder is comparable to N-1 and N-2 powders in terms or primary particle diameter, 2) P-1 powder has opposite electrification polarity to N-1 and N-2 powders, and 3) the electrification of P-1 is nearly equal to that of N-1 and N-2 powders. These results suggest that PMMA powder, without aggregation, is in contact with iron powder at an equal probability. They also suggest that the electrification of mixed powder can be easily controlled with high precision by using a mixing ratio of ultrafine powders having equal particle diameters and different polarities.



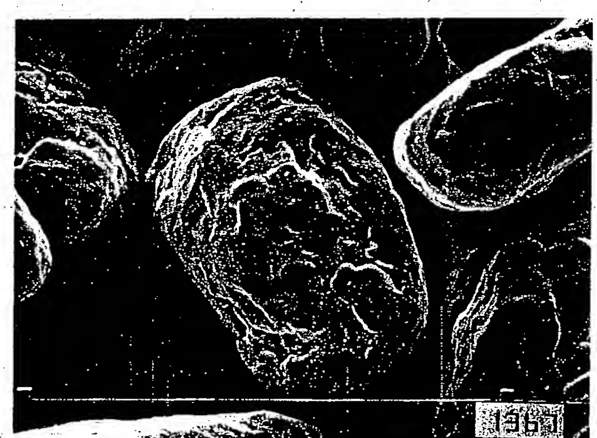


Photo-1 SEM photographs of the mixture of iron and PMMA powders before and after blowing off.

Electrification characteristics

Acrylic ultrafine powder consists of very loose particles. It disperses readily in organic powder, including plastic, and various other types of powder such as pigment, ceramics, and metal in a simple process of mixing and dispersion. This outstanding dispersion is derived from a unique electrification phenomena. The contact electrification of PMMA ultrafine powder to iron powder has been investigated in the air phase by the blow-off technique. Figure 4 shows schematically the principle of measuring the contact electrification of powder by the blow-off technique. A carrier for electrophotographs oxidation treated iron powder with a particle diamter of 44 – 74 μm (trade name, TEFV-200/300, Japan Iron Powder) is mixed with PMMA ultrafine powder at a fixed ratio, and shaken in a polyethylene bottle. The misture was then used as the measuring sample. Three hundred milligrams of the sample powder was placed in a Faraday cage. Only the PMMA particles were blown off through a wire net using nitrogen gas at a pressure of 1kg/cm^2. A charge equivalent to and of an opposite code to it was taken away by PMMA powder left in iron powder remaining in the cage. It electrified a capacitor (capacity C) that was connected to the cage. Pressure V was measured on both ends to determine the total blow-off charge Q, using the following equation:

$$Q_1 = CV \qquad (1)$$

Blank charge Q_2, which was obtained by blowing off the iron powder alone under the same conditions, was measured to calculate the contact electrification of PMMA powder per unit weight Q/m to μc/g using the following equation:

$$Q/m = (Q_1 - Q_2)/m \qquad (2)$$

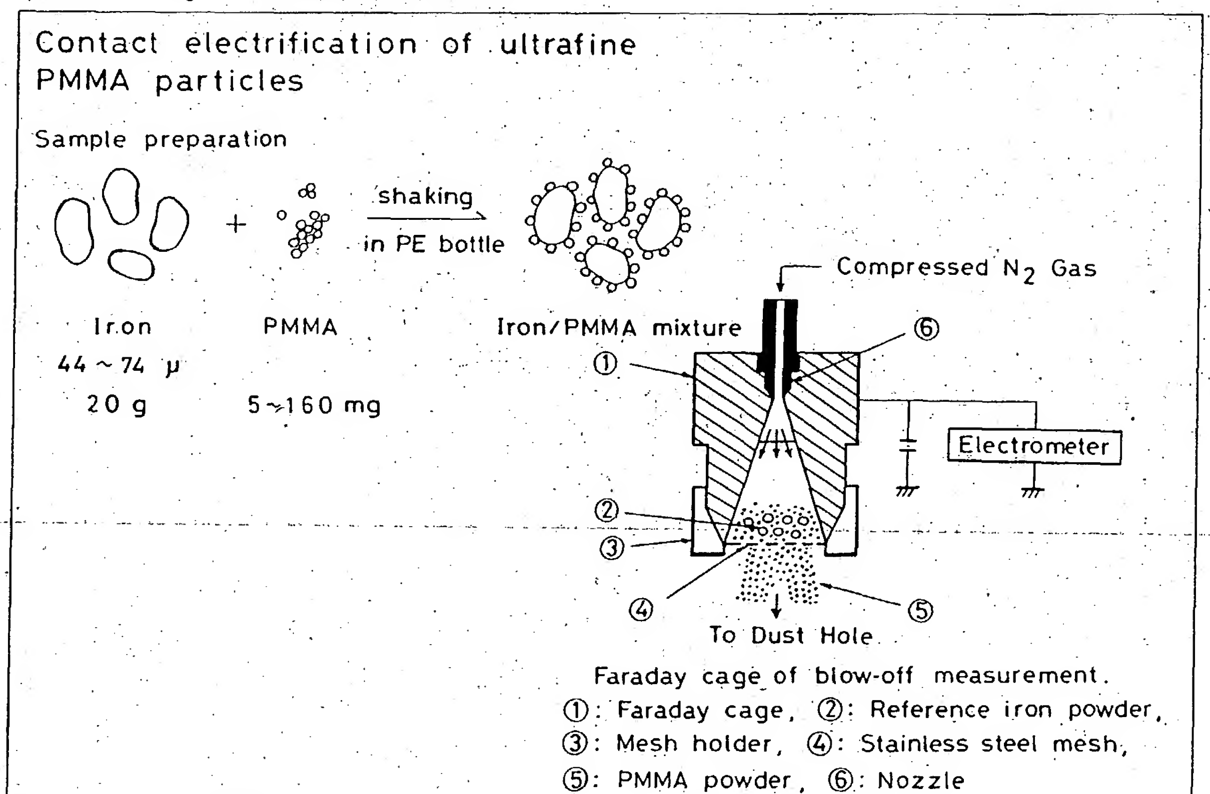
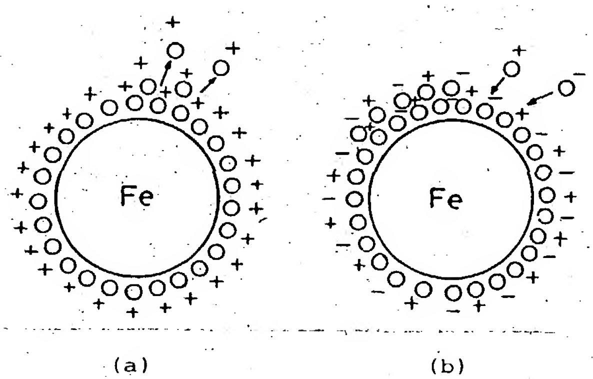


Fig. 4 Faraday cage of blow-off measurement.

(3) Electrification behavior of PMMA mixed powder near $\eta m = 0$

SEM shows that PMMA mixed powder adheres uniformly to the surface of iron powder just like unmixed powder. Figure 8 shows a particle adherence model of a mixture of positively and negatively charged PMMAs. Since the PMMA particles are isolated, they adhere to the surface of iron powder electrostatically, whether electrification polarity is positive or negative. However, repeated mixing of PMMA powder with iron powder increases the probability of adjacent particles having opposite polarity. This suggests that particles of a positively and negatively charged PMMA mixture adhere more uniformly to the surface of iron powder than do single polarity particles due to the lack of repulsion between particles, thus stabilizing adherence. Therefore, the use of a positively and negatively charged PMMA powder mixture makes it possible to coat the powder body with multilayers of PMMA powder. Iron powder coated with a PMMA mixture that is strongly charged with positive and negative electricity had difficulty adhering to a glass mortar and the walls of a polyethylene bottle. Figure 9 shows why. Agate and polyethylene between positively charged P-1 and negatively charged N-1 and N-2 come into contact with the positively and negatively charged PMMA mixture that covers the surface of the iron powder.

As a result, the positive and negative charges generated counteract each other. The contact surface appears as if no charges were generated. If these phenomena are utilized, PMMA powder can be used to prevent the friction electrification of dust.



(a): All of the PMMA particles have the same charge polarity.
(b): Half parts of the PMMA particles have the different charge polarity.

Fig. 8 Schematic diagram of PMMA particles adhesion to iron particle surface

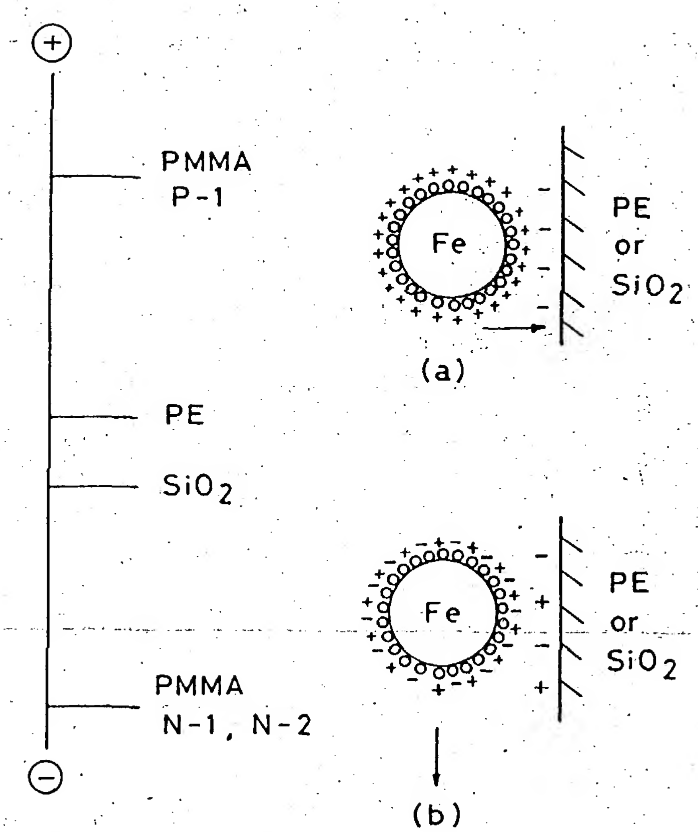


Fig. 9 Contact electrification series and adhesion characteristics of iron particle covered by the PMMA particles.

PMMA powder	composition	surface treatment	Mw	Tg (°C)	PH
P-1	MMA 100	DMA*	360000	130	7.2
N-1	MMA 100	Zn salt	360000	130	6.8
N-2	MMA 80 DVB 20	Zn salt	cross linkage	–	6.5

Table 4 Characteristics of ultrafine PMMA powder used in this experiments

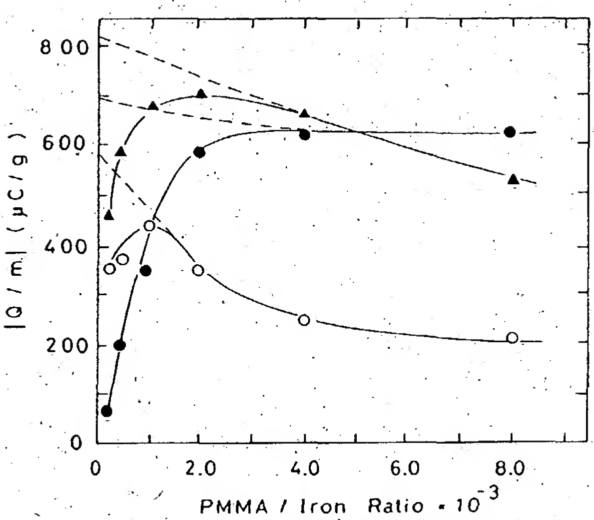


Fig. 5 Relation between blow-off charge and PMMA/Iron ratio.

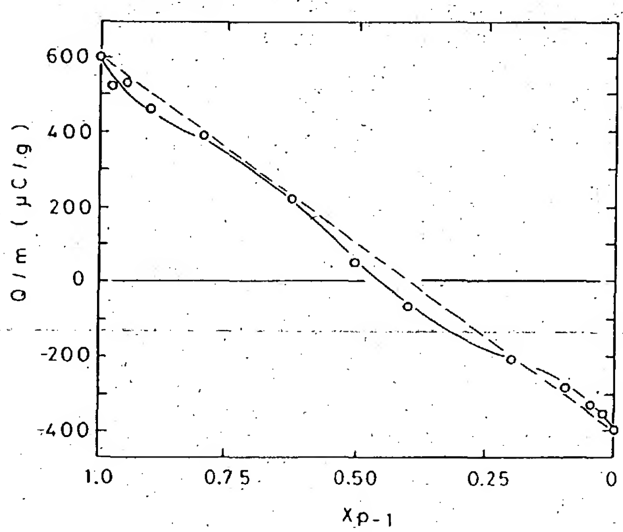


Fig. 6 Relation between blow-off charge and friction of P-1 (Xp-1) in (P-1)/(N-1) mixed powder.

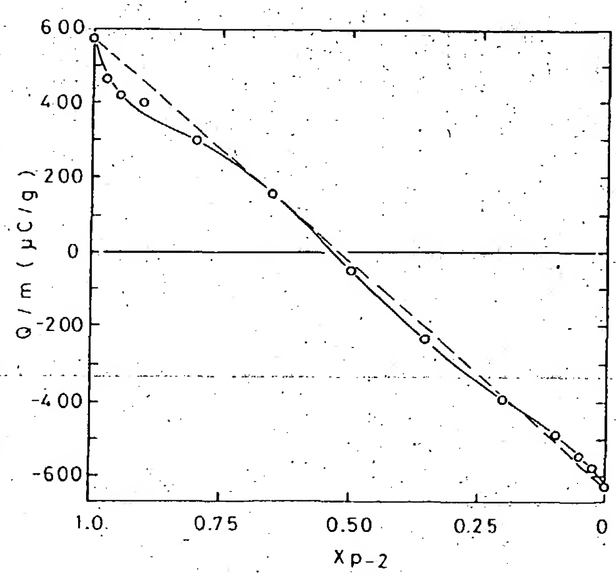


Fig. 7 Relation between blow-off charge and friction of P-1 (Xp-1) in (P-1)/(N-2) mixed powder.

Tap filling behavior of mixed dust

Figure 10 shows the tap filling behavior of a mixture of 5 μm-diameter polyethylene (PE) fine powder and 0.4 μm-diameter PMMA powder. PE powder was mixed with PMMA powder at a fixed mixing ratio, and PMMA particles were made to adhere to the surface of the polyethylene. This was used as a sample. Coating the surface of PE powder with PMMA makes it easier to increase the ratio of PMMA powder to PE powder, compared to polyethylene powder alone. The best filling ratio was obtained when polyethylene was completely coated with PMMA (PE/PMMA = 100/35). During tap filling, the PE fine powder was strongly electrified by friction with the PMMA tube, resulting in the powder splashing out of the tube. This phenomenon does not occur when PE powder is coated with PMMA. PE powder alone produces many voids during tap filling, since the particles do not loosen readily due to strong aggregation. PE powder coated with PMMA particles make tap filling easier, since the PMMA particles weaken the aggregation of dust and act as individual, void-reducing particles.

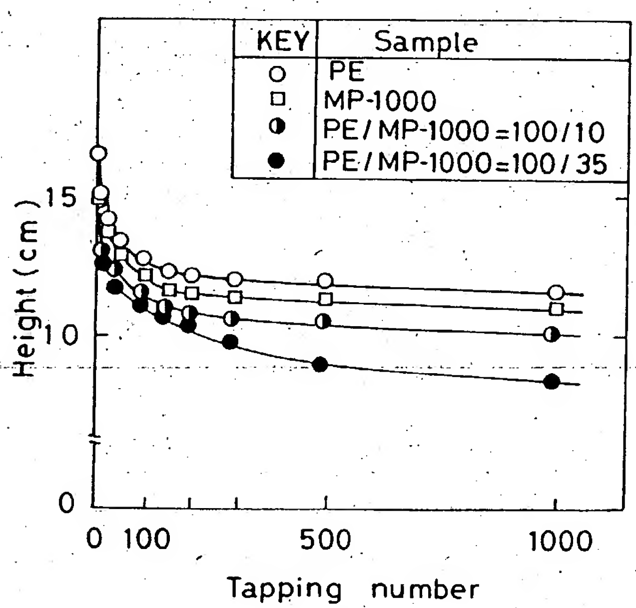


Fig. 10 Tap filling behavior of PE/PMMA mixed powder.

Attitude toward surface improvement

A mixture of acrylic ultrafine powder and dust is not treated as a conventional binary system, but as a single system of modified dust with an acrylic ultrafine particle coated surface. The advantage of a dry blend system with a modified dust surface in which friction electrification is utilized is that the individual particle surface can be modified without damaging the shape or grain size of the particles by mixing lightly. Photograph 4 shows PE fine powder mixed with PMMA particles. The particle diameter or the powder whose surface is to be modified should be larger than that of the acrylic particles. If the diameter is at least 10 times larger, any shape can be used. The type and amount of PMMA particles used depends upon the application. Besides their application in dry blend microcapsulation, it is important that new applications be found that take advantage of the market effect that small amounts of PMMA can have.

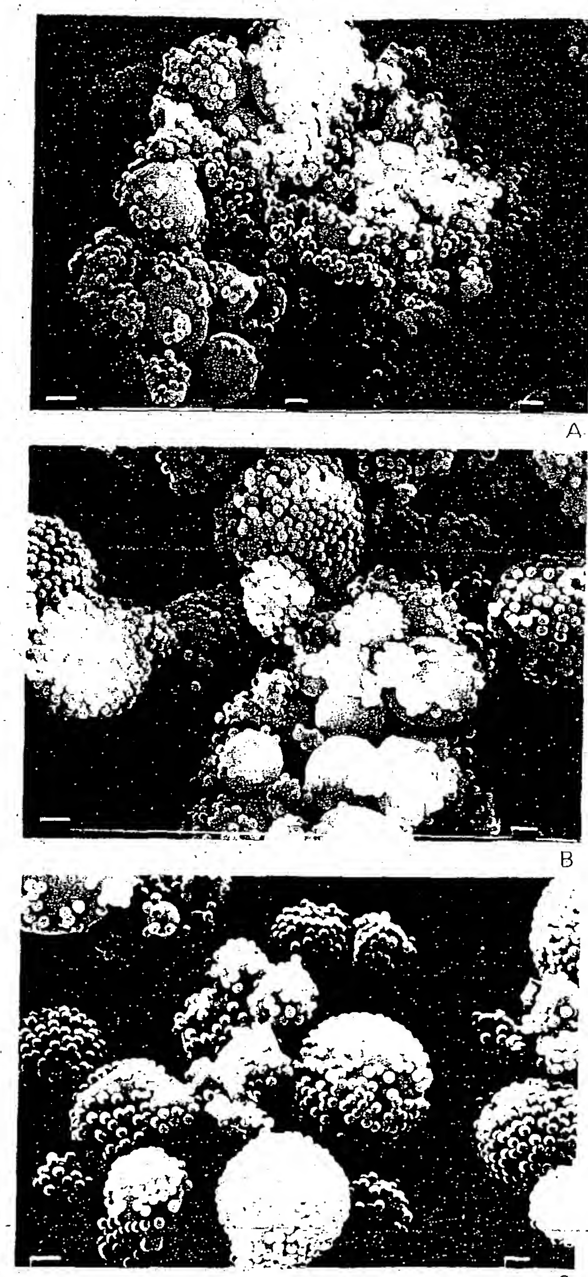


Photo-4 SEM of PE fine powder mixed with PMMA particles.
Ball mill mixing
A: 0 min. B: 5 min. C. 30 min.

Applications

Toner additive

Demands for PMMA particles are increasing as additives for binary system toners for electrophotographic development. Photograph 2 shows a magnified toner. PMMA particles are uniformly adhered to the surface of the toner. PMMA particles are added at the ratio of 1% or less to the toner, producing the following effects; 1) they eliminate cleaning, 2) they lengthen the life of the toner, and 3) they do not impair sensitive materials, or inhibit filming. Fig. 11 shows changes in the electrification of a toner resulting from the amount of PMMA powder found when a toner is mixed with positively and negatively charged PMMA powders and a mixture of two PMMA types with different electrification polarities (close to $\eta m = 0$). The addition of a small amount of PMMA powder markedly changes the electrification of the toner. The electrification measured develops additivity when 10% or less PMMA powder is added. Analysis of the lap density of a PMMA powder and toner mixture shows that both initial (ρ_o) and final bulk densities (ρ_∞) tended to be lower than those of the toner alone, as shown in Fig. 12. Toner bulk tends to increase with poorer flow simply by adding a small amount of PMMA powder. In addition, interesting results have been obtained by adding PMMA powder. They include: 1) cleaner copies, 2) fog prevention, and 3) less toner consumption. Traditional fine powder such as silica is strongly dependent upon humidity. PMMA powder is less humidity dependent, because it does not absorb water. Recently, positively charged PMMA powder has been used as an additive for positively charged toners for organic sensitive materials (OPC).

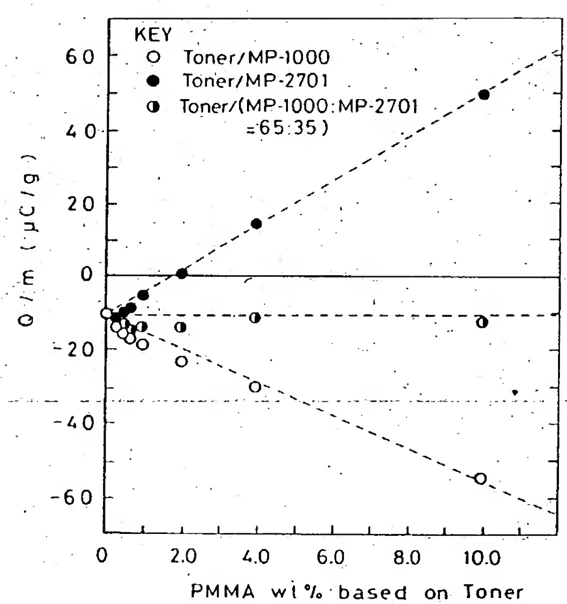


Fig. 11 Relation between blow-off charge and weight percent of PMMA in Toner/PMMA mixed powder.

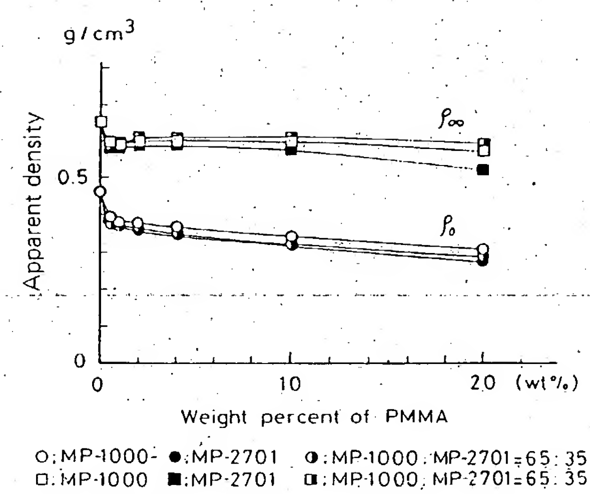


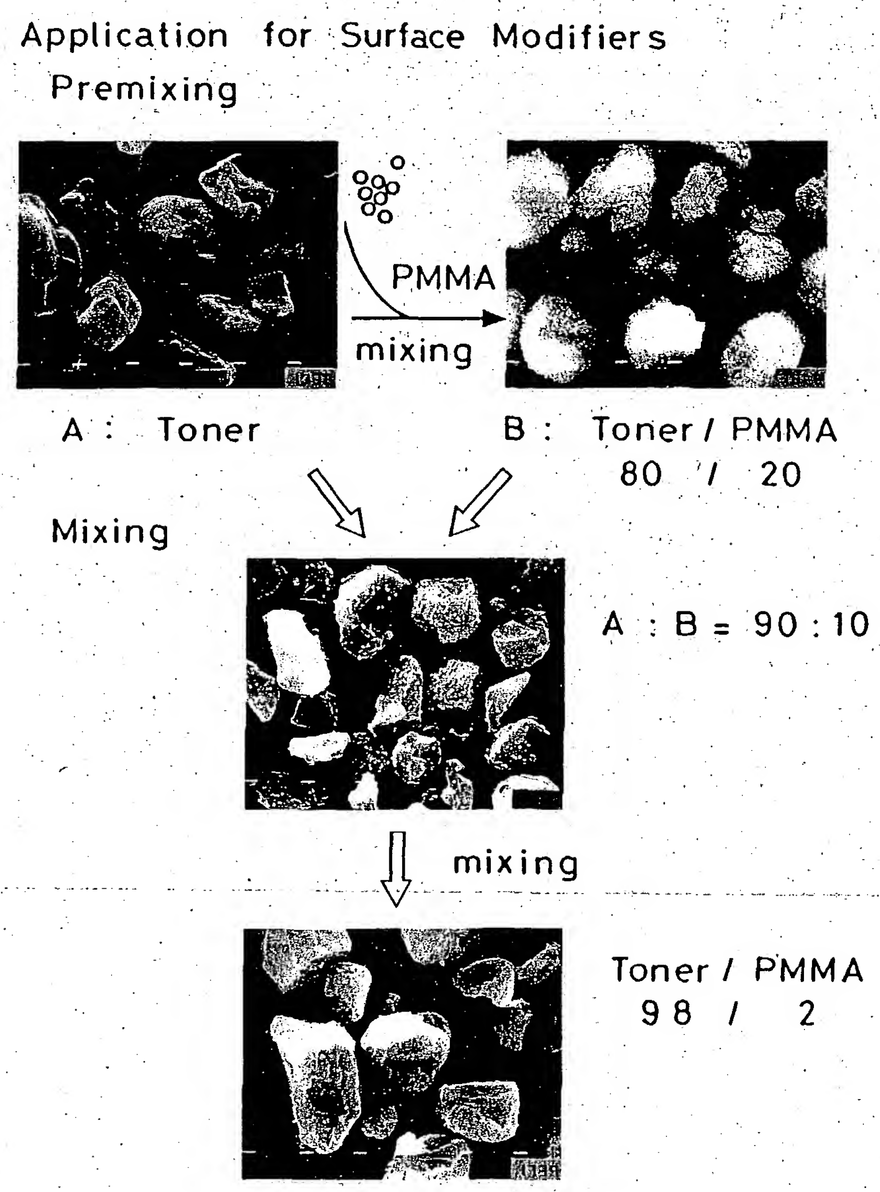
Fig. 12 Relation between apparent density and weight percent of PMMA in Toner/PMMA mixed powder.

Dispersion characteristics of acrylic ultrafine powder

In a mixture of acrylic ultrafine powder and a powder having particles 10 times the diameter, acrylic ultrafine particles uniformly adhered to the surface of the particles of the recipient powder when lightly mixed just enough to generate friction electrification.

Like a toner additive, the addition of only 1% or less acrylic ultrafine particles to the toner has a marked effect. In this case, the presence of aggregated acrylic ultrafine particles in a product has an adverse effect on th performance of the toner. Therefore, it is essential that the acrylic ultrafine particles be dispersed more uniformly.

To do this, the ratio of the surface of the toner particles that needs to be completely coated with acrylic ultrafine particles must be determined. The acrylic ultrafine particles are then premixed in a Henshell mixer to prepare seed particles.



Pigment dispersion

Dispersibility between pigments is improved by adding PMMA ultrafine particles to the pigment to control their charging capability. A small amount of positively charged PMMA ultrafine powder is added to titanium oxide (negative charge) and mixed with the binder. This mixture is less viscous and less thixotropic than titanium oxide alone.

Positively charged PMMA ultrafine powder is added during incorporation of titanium oxide into the organic pigment as a color lightener. Thus resulting in uniform, sharp colors.

Binder additive for precision casting molds

The viscosity of the slurry can be adjusted by adding PMMA ultrafine powder when making precision molds by the lost wax process. Such molds are free of rough surfaces, thus eliminating burrs on the metal castings.

Binder for molding powder

MP-1000 can be used as a binder for molding powder by making low-softening acrylic ultrafine powder adhere uniformly to inorganic powders, and using either electrostatic or thermal pressure coating.

Roughener

The surface of the film is roughened by applying an aqueous binder to which acrylic ultrafine particles of similar diameter have been added. When these particles are placed in layers, their slipperiness increases, and they can be used to treat the backs of tape. Interference light appears in about 0.4μm diameter particles when they are exposed to light, giving them a unique color.

Paper processor

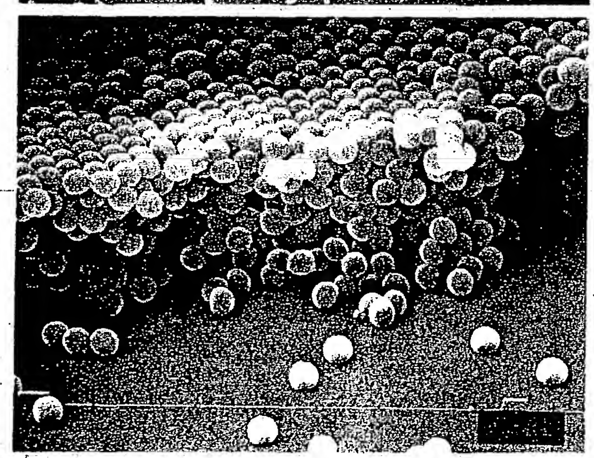
When PMMA particles and colloidal silica are mixed with an aqueous binder, and applied to processed paper, the silica accumulates in the gaps between the PMMA particles, thus preventing ink from seeping through the paper.

Conductive filler

Conductive fine powder with a low specific gravity was developed to permit the surface of fine powder to be electro-plated.

Other applications

These include flow modifiers, blocking inhibitors, antistatic agents, dispersion adjuvants, surface protection agents, fillers, ceramic binders, base materials for cosmetics, toners, powder pigments, molding materials, filtration adjuvants, testing (scale) agents, gelatinizers, flocculants, carriers for fixing ultrafine particle metals, catalysts, enzymes, and retainers for use in medicines, agricultural chemicals and perfumes.



Microcapsulation by dry blending

Attempts have been made to microcapsulate powder utilizing the friction electrification characteristics of PMMA particles. PMMA particles unifomly adhere to the surface of spherical powder by friction blending. The PMMA particles are subjected to shearing, impact, and compressive stresses for film application. A dry blending type microcapsular (Nara hybridization system), which has attracted a lot of attention, was recently developed. This system greatly reduces processes microcapsulation time compared to automatic mortar and ball mill processes, and forms a uniform film.

Figure 13 shows a schematic diagram of this system. Photograph 2 shows PMMA powder mixed with polystylene gel powder (mean diameter of particles, 17μm). Photograph 3 shows the microcapsulation of the same powder. The PMMA particles form a conti*nuous film over the surface of the polystylene gel* particles without causing any particle deformation. It is particularly interesting to note that PMMA particles that soften at 160°C or above form a film more *easily. With this method, the thickness of the micro-*capsule film is controlled by the diameter of the acrylic particles that adhere to the surface of the capsules. The capsulation processes consists of repeated cycles of coating the capsules with powder and filming.

Thus, the compounding of powdered materials will become easier if this method is used. It may be possible to develop a compound material having a multilayer structure separated by binder layers if PMMA particles can be fixed to materials having particle diameters ranging from several μm to several hundred μm, such as pigment, inorganic powder, metal fine powder, ceramics, and organic fine powder, using the dry blending technique. In this case, the material is capsuled with acrylic particles, and the procedure repeated. Additional applications and further research in this field will be the focus of attention in the future due to the virtually unlimited combinations of materials possible.

Another applications is slow-release micro-capsula-

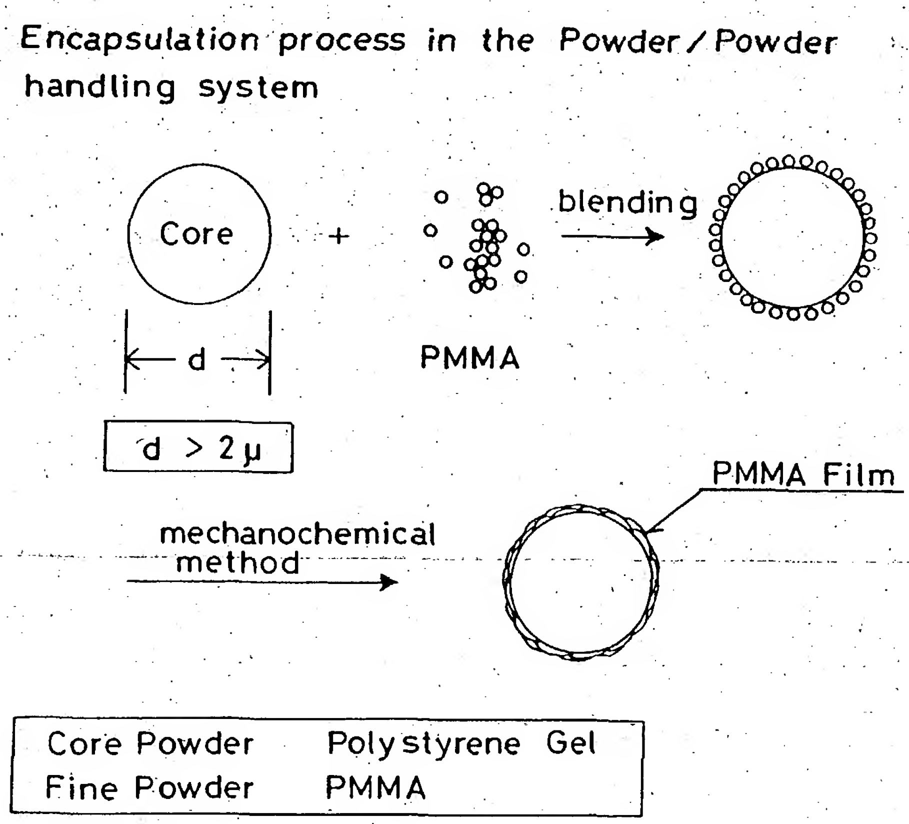


Fig. 13 Schematic diagram of encapsulation process in powder/powder handling system.

tion. Figure 14 shows a schematic diagram of the manufacturing method. Porous powder is impregnated with liquid, and turned into film with acrylic particles. Cellulose porous powder is impregnated with methyl salicylate, and capsulated with 0.25 μm-diameter titanium oxide and 0.4μm-diameter PMMA particles, which produces a poultice. When cellulose porous powder is microcapsuled with PMMA particles alone, fusion occurs between the powders, and a film is produced. This is because PMMA particles dissolve in methyl salicylate. The use of titanium oxide with PMMA particles makes capsulation possible because of the anchoring effect. Studies on slow-release microcapsulation, which include the impregnation of porous powder with flavorings, medicines, agricultural chemicals, and animal feed and its microcapsulation, have already begun.

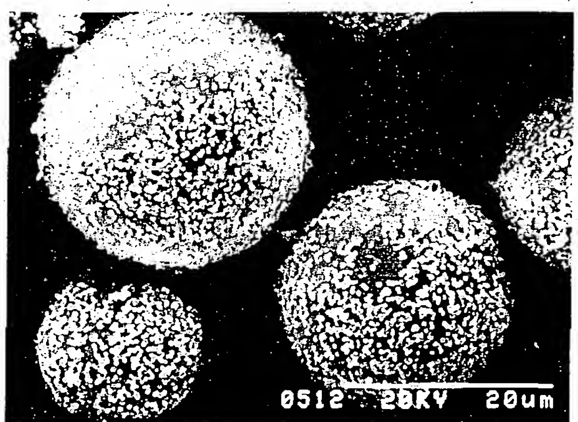


Photo-2 PMMA particles adhered to the surface of polystyrene gel powder

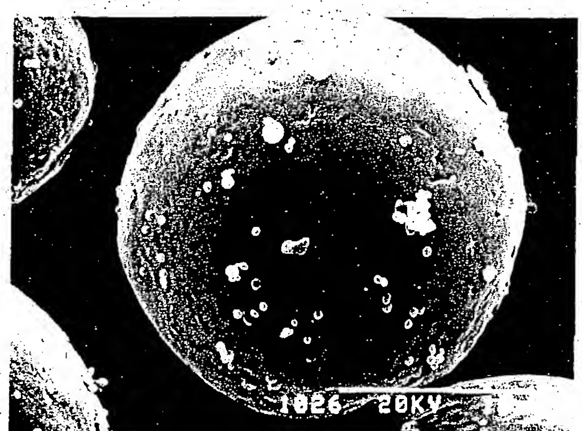


Photo-3 Surface of polystyrene gel particles covered by the PMMA continuous film.

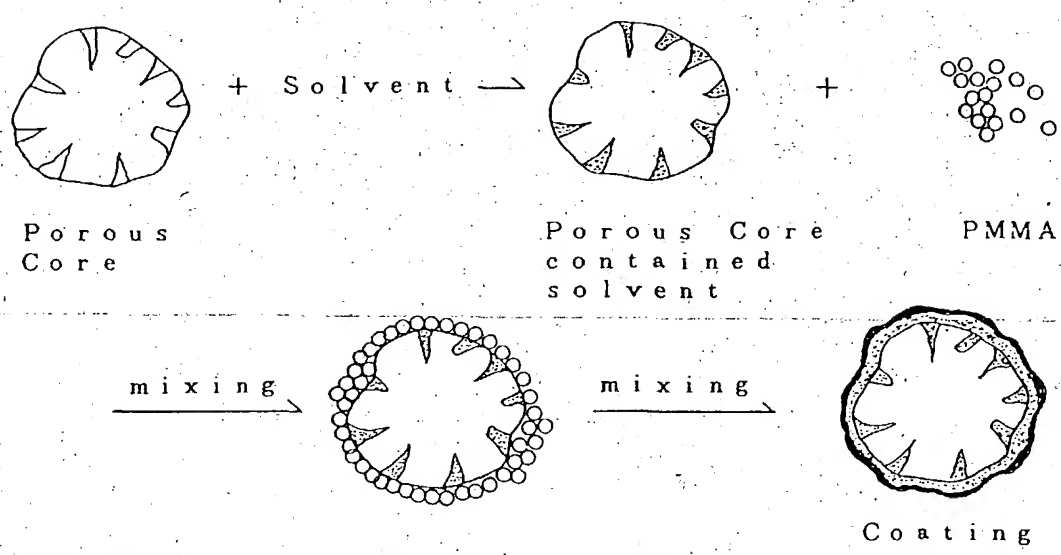


Fig. 14 Schematic diagram of the manufacturing method for slow-release micro-capsulation.

Porous sheet application

Porous sheets and films can be made by taking advantage of the moldability characteristics of acrylic polymer.

When microcapsulated spherical powder with the surface coated with acrylic particles by dry blending is heat pressed, the acrylic particles on the surface are fused to form a strong porous film (photograph 5). This film has the following advantages: 1) the diameter of the pores is controlled by the diameter of the particles of the microcapsuled powder, and 2) the path of the pores is lengthened. The substances such as enzymes and catalysts that are heat sensitive or are spoiled by organic solvents can be stabilized by fixing them to acrylic particles and forming a film on their surface. This can be applied to disposable cartridge type filters, medical reagents for diagnosis, and affinity chromatography.

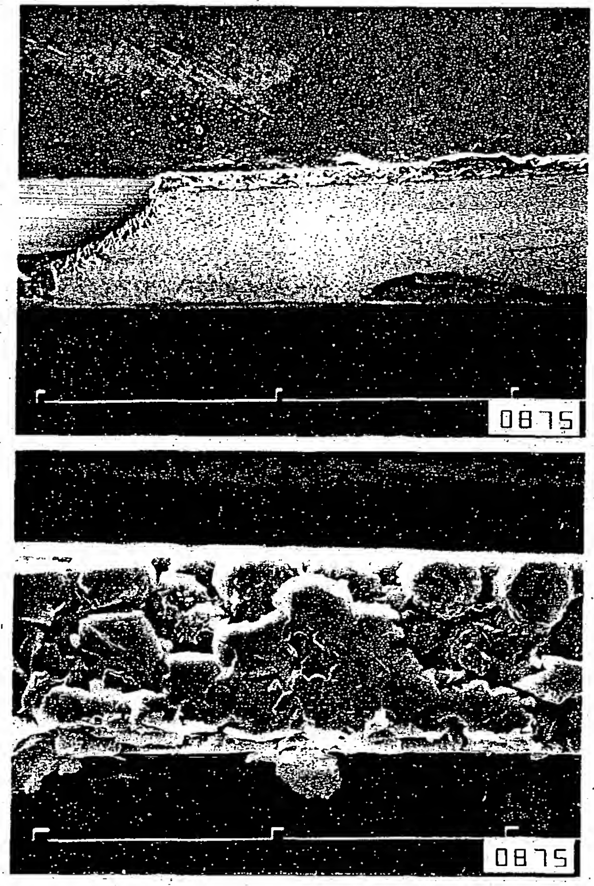


Photo 5 SEM of the porous film made from microcapsulated spherical powder with the surface coated with acrylic particles.